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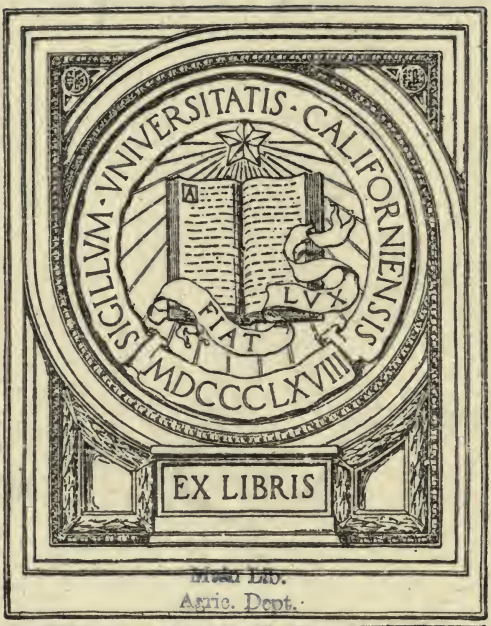

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United States Department of Agriculture,

BUREAU OF CHEMISTRY—Circular No. 27.

H. W. WILEY, Chief of Bureau.

COOPERATIVE WORK ON FATS AND OILS, ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1906.

By L. M. TOLMAN,
Associate Referee on Fats and Oils.

I. PROVISIONAL METHOD FOR THE TITER TEST, ADOPTED IN 1905.

After two years of cooperative work, the following method was recommended and adopted by the Association of Official Agricultural Chemists at its meeting November 16–19, 1905, as the provisional method for the titer test:

METHOD.

Weigh 75 grams of fat into a metal dish and saponify by using 60 cc of 30 per cent sodium hydrate (36° Baumé caustic soda) and 75 cc of 95 per cent by volume alcohol, or 120 cc of water. Boil down to dryness, with constant stirring, to prevent scorching. This should be done over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc of 30 per cent sulphuric acid (25° Baumé sulphuric acid) to free the fatty acids, boil until they form a clear, transparent layer, and then wash the fatty acids with boiling water until free from sulphuric acid. Collect the fatty acids in a small beaker and place on the steam bath until the water has settled and the fatty acids are clear, then decant them into a dry beaker, filter, using a hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° C or 20° C above the expected titer and transfer to the titer tube, which is 25 mm in diameter and 100 mm in length (1 by 4 inches) and made of glass about 1 mm in thickness. This is placed in a 16-ounce, salt-mouth bottle of clear glass, about 70 mm in diameter and 150 mm high ($2\frac{4}{5}$ by 6 inches), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. The thermometer, graduated to 0.1° C, is suspended so that it can be used as a stirrer, and the mass is stirred slowly until the mercury remains stationary for thirty seconds. The thermometer is then allowed to hang quietly, with the bulb in the center of the mass, and the rise of the mercury observed. The highest point to which it rises is taken as the titer of the fatty acids. The titer must be made at about 20° C for all fats having a titer above 30° C and at 10° C below the titer for all other fats.

The fatty acids are tested for complete saponification as follows:

Three cc of the fatty acids are placed in a test tube and 15 cc of alcohol (95 per cent by volume) added. The mixture is brought to a boil and an equal volume of ammonia (0.96 sp. gr.) added. A clear solution should result, turbidity indicating unsaponified fat.

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STANDARD THERMOMETER.

A standard thermometer of the following description was also adopted:

The thermometer shall be graduated in one-tenth degrees from 10° to 60° C, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm below the 10° mark. The 10° mark is to be about 3 or 4 cm above the bulb, the length of the thermometer being about 15 inches over all. The bulb shall be of Jena normal 16^{111} glass and the thermometer annealed for seventy-five hours at 450° C. The bulb shall be of moderately thin glass (so that the thermometer will be quick acting) and be about 3 cm long and 6 mm in diameter. The stem of the thermometer shall be 6 mm in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation clear-cut and distinct, but quite fine. The thermometer shall be furnished with a felt-lined case.

It was recommended, however, that further study be made of the method to be employed in drying the fatty acids.

II. DIFFERENTIATION OF THE "COLD TEST" AND THE "CLOUD TEST."

As a result of correspondence with chemists interested, a collection of the various methods used in this country in making the cold test has been made. A study of these methods shows that there seem to be two well-defined tests commonly classified under the title of "cold test." One is the temperature at which an oil becomes turbid because of the crystallization of *some* of the constituents of the oil, and the other is the temperature at which an oil will flow. In consideration of the fact that the cloud test very well describes the clouding due to the separation of the crystals, it would seem to be better to limit the meaning of "cold test" to that class of tests where the temperature at which the oil will flow is determined, and "cloud test" to the class of tests in which the temperature of clouding is obtained. This will enable us to convey a definite idea when we speak of "cold test" and "cloud test."

There seems to be no doubt that these two tests represent different determinations. The cloud test gives the temperature at which the more solid fats or oils begin to crystallize, and when we consider that all oils are made up of substances varying widely in their crystallizing points, it would seem hardly possible that the information given by this test could have the same meaning as a determination of the congealing point of the whole oil, which is the information given by the cold test. Moreover, there are two classes of oils to consider—first, the edible oil, which must remain clear at a certain temperature, and, second, the lubricating oil, which must flow at a certain temperature. A test like the "cloud test" is the one to be applied to the edible oils, while the "cold test," which gives information regarding the temperature at which the oil will flow, will be the only satisfactory test to apply to lubricating oils.

COLD TEST.

There seem to be several objections to the method for the cold test as given by the Prussian State Railway Direction, some of which are based on its complications, although it seems that the method might be readily modified so as to be extremely practical and rapid. The chief objection, however, is the fact that the oil is not stirred in any way while cooling, and it is a well-known fact that oils can be cooled to a considerable degree below their crystallizing points if kept perfectly quiet, while lubricating oils in actual use are in motion. The chief advantage of the method is that it eliminates the personal equation as to whether the oil flows or not. It seems to be the consensus of opinion, however, that a simpler method, such as that used by the Pennsylvania Railroad and by the United States Navy Department, with perhaps some slight modification in the manner of carrying out the test, would satisfy every requirement of accuracy and speed.

A number of valuable suggestions have been brought out by correspondence with the various chemists. W. H. Low, of the Cudahy Packing Company, says: "The trouble with all flow tests is that the solidified oil may move as a piston, owing to the sides of the container being warmer than the body of the oil." This trouble is overcome to a certain extent by the scheme suggested by J. P. Millwood, of the Brooklyn Navy-Yard, of insulating the bottle with a holder of asbestos pipe covering. It seems to the referee, however, that even this insulating of the bottle might be insufficient in many cases, and that perhaps warming up in a bath not far from the flowing temperature would give better results. It seems also that the oil should be stirred as it is cooled, in order to give it a more uniform texture and make the melting more even. Oil is a mixture of fats of various crystallizing points, and only by continued stirring while cooling can the various constituents be uniformly mixed.

The need of a special thermometer which can be read without removing from the bottle was noted by Robert Job, of the Philadelphia and Reading Railroad, and by J. P. Millwood, of the Brooklyn Navy-Yard. The latter thus describes the thermometer used by him: "The special thermometers used are graduated in degrees from 0° to 100° F and are 18 inches long, with the zero point about 7 inches above the bulb, which brings it outside the bottle."

The importance of the element of time in the test has been emphasized by several chemists, and it is on this point that we find the greatest divergence in practice. The experience of many indicates that definite conditions as regards time will have to be made. It is possible, however, that in a method requiring continued stirring the time factor would not be so important.

Thomas Gladding suggests making the cold test by placing the oil in

a bottle which is placed inside another bottle, thus surrounding it with an air jacket. This is set in a bath of cold water. The oil is constantly stirred by a mechanical stirrer until it begins to thicken as shown by the slowing down of the stirrer. Mr. Gladding would have the temperature lowered very slowly and make the determination in much the same way as the titer of the fatty acids. He is, however, determining the congealing point, which is not the determination made in the cold test as ordinarily practiced, i. e., the melting point of the mixed oils, and it is hardly to be expected that the congealing points and melting points will be the same.

In testing the lubricating oils, the oils should be dried, while in testing salad oils where it is desired that the oils remain clear it is evident that the water must not be removed.

CLOUD TEST.

The cloud test is given by Dr. Manns as follows:

1. The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

2. The oil must be heated to 150° C over a free flame, immediately before making the test.

3. There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice, and water.

The test is conducted as follows: The oil is heated in a porcelain casserole over a free flame to 150° C, stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce oil bottle, which must be perfectly dry. One and one-half ounces of the oil is sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled by immersion in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few moments. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within 1° F can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit.

The oil must be tested within a short time after heating to 150° C, and a retest must always be preceded by a reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

This method seems to be entirely satisfactory except that the drying would not be legitimate when the test is used on salad oils, as moisture would affect the clearness of these oils as much as crystallized fats. If the cloud test, as given by Dr. Manns, can be substituted in the testing

of salad oils for the test as given by the New York Produce Exchange, it would be a great saving of time. It seems to the referee that a method in which the oil is allowed to remain perfectly quiet can never be satisfactory.

III. CONCLUSION.

To sum up, it appears from the correspondence that it is practically agreed that the cloud test and the cold test represent different methods and do not furnish the same information, but, as Dr. Dudley says, there is need for both tests; also, that the cloud test is suitable for salad oils and for testing lubricating oils when the temperature at which they cloud is desired, and that some modification of the flowing test must be used for testing lubricating oils. The work thus separates itself into two parts—first, a study of a method for lubricating oils, and, second, a method for salad oils.

As a basis, however, the following method for the cold test is offered as a starting point. This is practically the one used by J. P. Millwood, with a few added details suggested by the experience of others.

COLD TEST (MILLWOOD).

Warm the oil until all the stearin is dissolved and filter, through several thicknesses of filter paper, into a *dry* 4-ounce wide-mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the special cold-test thermometer previously described, and at every degree rise in the temperature the bottle is inverted; continue till the oil will run to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

The questions at issue on lubricating oils are—

1. Method to be used:
   (*a*) A flowing test?
   (*b*) A clouding test?
2. Preparation of oil for analysis:
   (*a*) Shall it be dried, and how?
   (*b*) Shall it be filtered?
3. Method of cooling:
   (*a*) Shall it be stirred until solid?
   (*b*) Shall it stand a definite time; and if so, how long?
4. Method of melting:
   (*a*) Shall it be allowed to warm up at room temperature?
   (*b*) Shall it be warmed up in a bath?

As regards salad oils—

Can the cloud test be used for the testing of salad oils such as winter cottonseed oil?

Cooperative work along the following lines is requested for the purpose of answering the questions enumerated above:

A number of samples of oil will be sent out by the referee to the various chemists to be tested—

1. By the method in use in the respective laboratories.
2. By the cloud test as given by Dr. Manns.
3. By the cold test of the Pennsylvania Railroad as modified by Millwood.
4. In regard to the other points at issue as far as is practicable.

Report of the results should be sent to the referee as soon as possible, as this is only a preliminary investigation. In the report make any suggestions or criticisms that may seem pertinent.

Approved:

JAMES WILSON,
Secretary of Agriculture.

WASHINGTON, D. C., *February 5, 1906.*

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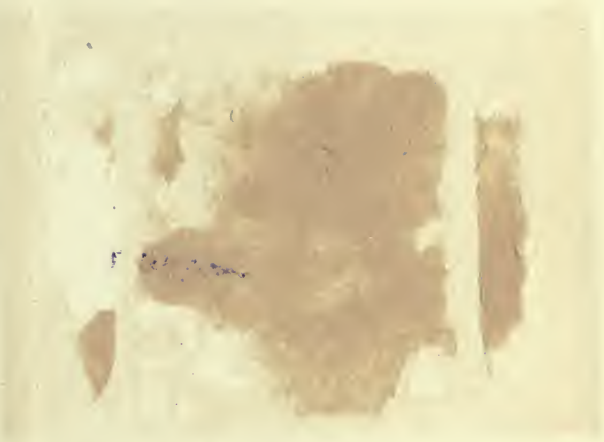
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